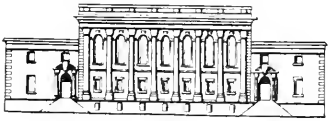

A STUDY OF DIPOLE MOMENT THEORY AND ITS IMPLEMENTATION

by

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A Study of Dipole Moments

All molecules, generally speaking, can be classified into two categories, depending upon the nature of the atoms which compose those molecules; they are either polar, possessing an electric dipole moment which exists in the absence of an applied field, or they are non-polar and do not possess the so-called permanent dipole moment. In order to understand the distinction between polar and non-polar molecules, it is necessary to clearly define the term electric dipole moment. Consider a bond between two atoms which differ in electronegativity so that there will be a center of negative charge around the more electronegative atom and a center of positive charge around the more electropositive atom. Because of this separation of charges, the bond possesses or can be called a dipole, an equal positive and negative charge $\mp Q$, separated by a distance r. Characteristically, the bond has a dipole moment, $\vec{\mu}$, a vector quantity having the magnitude Qr and the direction of the line joining the negative to the positive charge. The components of this vector quantity can be defined by letting x_i, y_i, and z_i be the coordinates of the charge Q so that

$$\mu_x = \sum_i q_i x_i \qquad \mu_y = \sum_i q_i y_i \qquad \mu_z = \sum_i q_i z_i \qquad (1)$$

If the net charge $\sum_i q_i$ is zero, $\vec{\mu}$ is independent of the

location of the origin. (In future references unless specified by → over the given letter, only magnitudes of vector quantities will be considered.)

Since dipole moment is defined as having the dimensions charge (q) x length (r), the units of μ can be calculated by considering 2 charges separated by 1 Å and possessing the magnitude of e, the fundamental electronic charge, 4.80×10^{-10} electrostatic units (e.s.u.). The dipole moment in this instance would be 4.80×10^{-18} e.s.u. cm. All dipole moments are on the order of 10^{-18} e.s.u. cm., and dipole moment values are expressed in terms of the Debye unit (D), which is equal to 10^{-18} e.s.u. cm.

If a molecule having more than one dipole in different bonds is considered, the net dipole moment for the molecule is obtained by calculating the resultant of the vector addition of the moments for each individual bond. An example of such a procedure is illustrated in Figure 1.

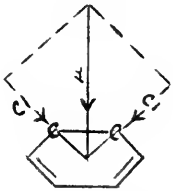


Fig. 1. Calculation of the Resultant for Orthodichlorobenzene

THEORY

Although the concept of dipole moment is quite simple, the theory concerning its experimental measurement is complex. In his classic treatise "Polar Molecules "

Pieter Debye developed one of the first equations through which dipole moments could be determined from experimental values. This equation relates dipole moment to dielectric constant as well as to other observable properties, molecular weight and density.[1]

The relationship of dielectric constant and dipole moment, fundamental to dipole moment theory, can be seen in the derivation of the Debye equation. In this derivation it is necessary to consider some fundamental electrostatic field relations as well as the theory of dielectrics.

If a fixed parallel-plate capacitor is considered, with a vacuum between the plates and a charge of $+\sigma$ per sq. cm. on one plate and $-\sigma$ on the other, the external electric field creates a field within the capacitor which has a magnitude

$$E_o = 4\pi\sigma \qquad (2)$$

and is directed perpendicular to the plates. The capacitance is

$$C_o = \frac{A}{4\pi d} \qquad (3)$$

with A equal to the area of the plates, d the distance between them. If the capacitor is then filled with a material substance (in liquid, solid, or gaseous state), the effect of the electrical field on the substance introduced will differ according to the nature of the substance. In a conductor transfer of electrons over distances which are large when compared with molecular dimensions occurs quite freely.

By definition, in a dielectric the charges are bound within the fairly rigid framework of the neutral molecule, and the electric field displaces the electrons over distances which are small, on the order of a molecular diameter. This electronic displacement induced in dielectrics by an electrical field is known as polarization.

The polarization of a dielectric is pictured in Figure 2; the field causes a separation of positive and negative charges in the dielectric.

Figure 2. Polarization of a Dielectric

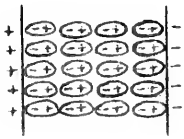
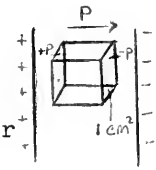


Figure 3. The Polarization Vector



When a dielectric is introduced to an evacuated cell, its effect will be to increase the capacitance by a factor ϵ, the dielectric constant, so that

$$C = \epsilon C_o \qquad (4)$$

where C_o is the capacitance of the cell in a vacuum. Concurrently, the electric field will be reduced so that

$$E = \frac{E_o}{\epsilon} \qquad (5)$$

Looking at Figure 2, it is easy to see how the dielectric causes a reduction in the electrical field; the dipoles in the dielectric are aligned against the field at the boundary between the dielectric and the capacitor so that overall field strength will be reduced.

In mathematical terms polarization is described in terms of a vector quantity $\vec{P}$, the dielectric polarization,

defined as dipole moment per unit volume. If a 1 cm. cube is placed between the plates of a capacitor (as in Figure 3), inducing a charge of +P on one face of the cube and a charge of -P on the other face, the total field will be reduced by a quantity $4\pi P$ so that equation (2) for the electrical field is replaced by

$$E = 4\pi(\sigma - P) \tag{6}$$

$$E + 4\pi P = 4\pi\sigma \tag{7}$$

In physical terms equation (7) results from the fact that a neutralizing charge $+4\pi P$ will flow through the circuit to the capacitor plates, the charge being equal and opposite in sign to that induced on the surface of the dielectric.

A new vector $\vec{D}$ has thus been defined with

$$D \equiv E + 4\pi P = 4\pi\sigma \tag{8}$$

and

$$\frac{D}{E} = \epsilon \tag{9}$$

This vector is known as the electric displacement. From the above relationships it follows that

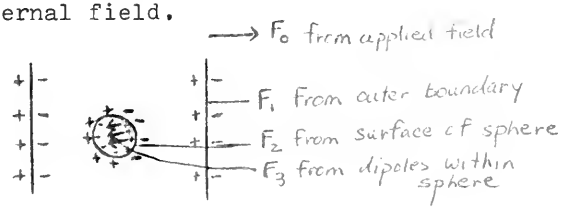
$$\epsilon = 1 + \frac{4\pi P}{E} \tag{10}$$

In a vacuum where $P = 0$ and $D = E$, $\epsilon = 1$. When a dielectric is introduced into the capacitor, ϵ is by definition > 1.

The vectors $\vec{D}$ and $\vec{E}$ represent classical external field intensities. It is also necessary to consider the field intensity F at the site of the molecule when the

capacitor is filled with a dielectric. Figure 4 is helpful in the consideration of the internal field.

Figure 4. Components of the Internal Field



In Figure 4 a homogeneous field is created by equally distributing a system of charges between the plates of a capacitor. On a molecular level the force F acting upon a particle of unit charge can be viewed as consisting of 4 parts.

$$F = F_0 + F_1 + F_2 + F_3 \qquad (11)$$

The component $F_0 + F_1$ is due to the electrical field distributed uniformly between the plates and to the so-called depolarization field induced in the dielectric at the interface between the capacitor plates and the dielectric material. Thus

$$F_0 + F_1 = D - 4\pi P = E + 4\pi P - 4\pi P \qquad (12a)$$

as determined from equations (2) and (8).

F_2 and F_3 are related to the introduction of a sphere surrounding the particle. The sphere is small when compared to macroscopic quantities but larger than molecular levels. F_2, known as the Lorentz field, is due to the induced layer of charge on the boundary between the outer surface of the sphere and the dielectric material. The equation for F_2, first presented by Lorentz, is derived by letting

r stands for the radius of the sphere, θ the angle between r and P, and ω , a surface element (see Figure 5). The basic premise upon which this derivation rests is that "the magnitude of the normal component of the polarization vector is equal to the density of the induced charge on any boundary of the dielectric."[2] The force on the interior particle can be found by applying Coulomb's Law (the force between two charges is proportional to the product of the magnitude of the charges divided by the square of the distance between them) to each surface element of charge. At any point on the sphere, the density of the surface charge equals P_n , the normal of the polarization vector as stated above. P_n equals P cos θ from trigonometric calculations so that integrating over the entire surface

$$\int_{surface} \frac{P\cos\theta}{r^2} d\omega = 2\int_0^{\pi/2} \frac{P\cos^2\theta}{r^2} \cdot 2\pi r^2 \sin\theta \, d\theta = \frac{4\pi}{3} P \qquad (12b)$$

For a more complete derivation of this last equation, see Appendix I.

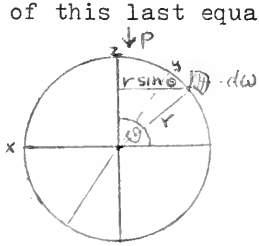


Figure 5.
Diagram for
Derivation of
F_2

The component F_3 is the force due to the dipoles within the small sphere. F_3 depends upon structure. If a reference point has symmetrical, cubical surroundings, the

dipoles within the sphere will align themselves parallel to each other, and

$$F_3 = 0 \qquad (12c)$$

F_3, however, is an extremely complicated function and cannot be easily evaluated. In this derivation it is assumed that $F_3 = 0$.

The total internal force can now be computed from equations (11), (12a), (12b), and (12c).

$$F = 4\pi\sigma - 4\pi P + \frac{4\pi P}{3}$$

According to equation (8), $D = 4\pi\sigma \equiv E + 4\pi P$. It follows that the internal field acting on a particle of unit charge is

$$F = E + \frac{4\pi P}{3} \qquad (13)$$

The assumptions which are made in the derivation of F in the previous paragraphs are quite large and must be considered when discussing the validity of equation (13) as an expression of the internal field. The ambiguity in the value of the F_3 term introduces a factor which can lead to erroneous results when the theory is applied experimentally. Since it has been found that $F_3 = 0$ for molecules which move totally independent of each other, as in the case of gases, applications of the internal field as defined above must be limited to gases and to dilute solutions where little molecular interaction takes place. Debye realizes this in his treatise:

> The only possible way to avoid this difficulty seems to be not to consider ... the ordinary measurements on liquids of comparatively high density, where the mutual interaction of the molecules is important, but to base the calculation on measurements of gases and perhaps diluted solutions, the molecules being mostly far enough apart so that their interaction may be neglected.[3]

Polarization, defined as dipole moment per unit volume, is a complex term and must be viewed more specifically in dipole moment theory. There are two different types of polarization, that due to the induction effect, and that due to the orientation effect. In a molecule where both effects are present, the total polarization P is equal to the sum of the polarization due to induction P_d and the polarization due to orientation P_o .

$$P = P_d + P_o \qquad (14)$$

The induction effect is seen in every molecule which is placed in an electric field. Dipoles are always induced in a molecule under the influence of an electric field, regardless of whether or not the molecule contains a permanent dipole. The electric field causes a separation of positive and negative charges. An additional orientation effect contributes to the polarization of molecules which are permanent dipoles. This orientation polarization is due to the fact that an electric field tends to align permanent dipoles in the direction of the field. It is evident that the P_o term is dependent on temperature; random motion of the

molecular dipoles will tend to oppose their alignment with the field. Since an increase in temperature results in an increased thermal motion and a greater randomness among the molecules, temperature and orientation polarization are inversely related.

Molecules exhibiting orientation effects are those which are permanent dipoles and which have permanent dipole moments; they are polar molecules. Since both induction and orientation effects are important in the total polarization for such molecules, both must be mathematically represented in dipole moment theory.

The mathematics of induction polarization was elucidated by O. F. Mosotti in 1850 and repeated by Debye in "Polar Molecules".[4] To determine P the magnitude of the dipole moment $\vec{m}$ induced in a molecule by an electric field must be considered. The average moment for one molecule is assumed to be proportional to the electric field F at the sight of the molecule, an assumption which Debye justifies by saying that it is "supported by experiment."[5]

$$m = \alpha F \qquad (15)$$

α is called "polarizability," the induced moment per unit field strength. Assuming that n is the number of molecules in 1 cc. and remembering that P is defined as dipole moment per unit volume (1 cc.),

$$P = nm = n\alpha F = n\alpha\left(E + \frac{4\pi P}{3}\right) \qquad (16)$$

According to equation (8) $D = E + 4\pi P$ and $\frac{D}{E} = \epsilon$. If the P term is eliminated between equation (8) and (16), the dielectric constant ϵ expressed in terms of α, the molecular polarizability can be found.

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi n\alpha}{3} \tag{17}$$

Equation 17 is known as the Clausius-Mosotti relation. It is more completely derived in Appendix II.

Considering α as a constant, according to equation (17), $\frac{\epsilon - 1}{\epsilon + 2}$ is proportional to n and thus to the density. If equation (17) is multiplied on both sides by molar volume, the quotient of molecular weight M and density ρ, it becomes

$$\frac{\epsilon - 1}{\epsilon + 2}\,\frac{M}{\rho} = \frac{4\pi\alpha}{3}\,\frac{nM}{\rho} = \frac{4\pi}{3}N\alpha \tag{18}$$

where N is Avogadro's Constant.

Debye defines $\frac{4\pi}{3}N\alpha = \mathcal{P}$, the molar polarization. $\mathcal{P}$ differs from P in that $\mathcal{P}$ has the dimensions of volume whereas P is the dipole moment per unit volume. $\mathcal{P}$, in fact, could be called molar polarizability.

So far, $\mathcal{P}$ expresses only the polarization due to the induction effect. Debye, in his treatise, also derives the term due to the orientation effect. In the absence of an applied field, the orientation in space of a dipole with reference to a fixed direction will be random and

the dipole will assume all possible orientations over a period of time. The presence of an electric field, however, causes the dipole to align preferentially in the direction of the field. Assume that the dipole moment makes an angle Θ with a field of strength F, The potential energy of the dipole, affected by thermal motion, will be

$$U = -\mu F \cos\Theta$$

If a solid angle ω in the direction of the dipole moment is considered, the number of molecules oriented within the angle ω in the presence of a field F can be determined by the Boltzmann equation (see Figure 6).

$$A \exp\left(\frac{-U}{kT}\right) d\omega = A \exp\left(\frac{\mu F \cos\Theta}{kT}\right) d\omega \qquad (20)$$

where A is a constant depending upon the number of molecules under observation and k is the Boltzmann constant. Since a continuously varying function is being studied, the average value of the dipole moment in the direction of the field of 1 molecule can be found from equation (21) .

$$\bar{m} = \frac{\int_0^{4\pi} A e^{(\mu F/kT)\cos\Theta} \mu \cos\Theta \, d\omega}{\int_0^{4\pi} A e^{(\mu F/kT)\cos\Theta} d\omega} \qquad (21)$$

which upon evaluation yields

$$\bar{m} = \frac{\mu^2}{3kT} F \qquad (22)$$

The $\mu \cos\Theta$ term in equation (21) is due to the fact that

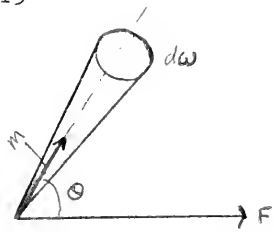


Figure 6. Diagram for Space Orientation of Dipoles

a specific molecule aligned in the direction of $d\omega$ has a component $\mu\cos\theta$ in the direction of the field. Substituting this value of $\bar{m}$ which is based on orientation polarization into equation (15), the effect of both orientation and induction polarization can be shown,

$$\bar{m} = (\alpha_o + \frac{\mu^2}{3kT})\ F \qquad (23)$$

and using the new value of

$$\alpha = (\alpha_o + \frac{\mu^2}{3kT}), \qquad (24)$$

known as Langevin-Debye equation, the molar polarization $\mathcal{P}$ can be reevaluated to include both effects.

$$\mathcal{P} = \frac{\epsilon - 1}{\epsilon + 2}\frac{M}{\rho} = \frac{4\pi}{3}\ N\ (\alpha_o + \frac{\mu^2}{3kT}) \qquad (25)$$

The only term in equation (25) which is ambiguous is the term α_o, having to do with the induction effect. The term $\frac{4\pi}{3} N\alpha_o$ can be considered to result from the distortion of the molecule brought about by the presence of an externally applied field. It has been previously mentioned that one effect of the field on the molecule is that of the displacement of electrons from their average positions within

the rigid framework of the molecule. This effect can be called the mean molecular electronic polarizability, α_e. In addition, another component of the term α_o is α_v, the mean molecular vibrational or atomic polarizability. The α_v term is due to a distortion of bond lengths and angles, or a distortion of the vibrational motions in the molecule because of the external electric field.

α_o, then, is the sum of two components $\alpha_e + \alpha_v$ so that equation (25) can be expressed

$$\mathcal{P} = \frac{\epsilon - 1}{\epsilon + 2} \frac{M}{\rho} = \frac{4\pi}{3} N \left(\alpha_e + \alpha_v + \frac{\mu^2}{3kT} \right) \qquad (26)$$

In experimental applications equation (26), developed by Debye, can be used to determine whether or not a molecule is polar and ultimately its permanent dipole moment. This can be done by measuring dielectric constant and density and plotting $\mathcal{P}$ against 1/T. Equation (26) can be expressed in terms of $\mathcal{P} = a + b/T$ where the intercept $a = \frac{4\pi}{3} N (\alpha_e + \alpha_v)$ and the slope $b = \frac{4\pi}{9k} N \mu^2$. A graph of $\mathcal{P}$ vs. 1/T should thus give a straight line plot and can be used to determine the polarity of molecules. Debye used the resulting plot to distinguish polar and non-polar molecules. In Figure 7 non-polar molecules form a horizontal line parallel with the x axis (they are non-dependent on temperature), whereas polar molecules illustrate T-dependence. Early application of the Debye theory can be seen in Figure 8,

Figure 7. $\mathcal{P}$ vs. T. Curves for Polar and Non-polar Molecules

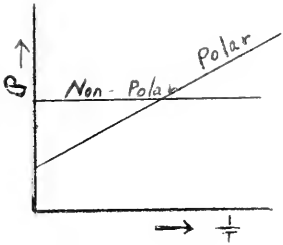
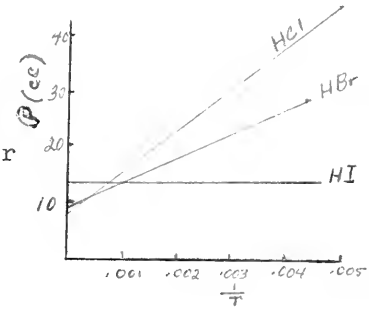


Figure 8. $\mathcal{P}$ vs. T. Curves for Hydrogen Halides



in which the polarity of HCl, HBr, and HI is studied.

In the previous discussion, the determination of dipole moments is limited to gases alone. Debye also extends his theory to make it possible for dilute solutions of polar molecules in non-polar solutes to be studied. It is important to remember that because of the limitations placed on Debye theory by his definition of F, the internal electric field, only gases and very dilute solutions can be studied by direct application of his theory.

In his study of solutions, Debye applied the Clausius-Mosotti equation to solutions by utilizing the concept of mole fraction and by considering the molar polarization $\mathcal{P}$ of both solvent and solute. He reasoned that

$$\mathcal{P} = X_1\mathcal{P}_1 + X_2\mathcal{P}_2 \qquad (27)$$

where X denotes mole fraction and subscripts 1 and 2 refer to the solvent and the solute respectively. Assuming this relation to be true, he then applied it to the Clausius-Mosotti equation:

$$\frac{\epsilon - 1}{\epsilon + 2} \frac{M_1X_1 + M_1X_2}{\rho} = X_1\mathcal{P}_1 + X_2\mathcal{P}_2 = \mathcal{P} \qquad (28)$$

$$\mathcal{P}_1 = \frac{4\pi N}{3} (\alpha_{v_1} + \alpha_{e_1}) \qquad (29)$$

$$\mathcal{P}_2 = \frac{4\pi N}{3} \left(\frac{\mu_2^2}{3kT} + \alpha_{v_2} + \alpha_{e_2}\right) \qquad (30)$$

$\mathcal{P}_1$ differs from $\mathcal{P}_2$ in that it is for a non-polar solvent, and subsequently the term containing the permanent dipole moment $\frac{\mu_2^2}{3kT}$ disappears in an expression for $\mathcal{P}_1$.

$\mathcal{P}_1$ can be calculated by assuming that for dilute solutions its value is approximately that of $\mathcal{P}_1^\circ$, the molar polarization for the pure solvent. It follows from equation (18) that

$$\mathcal{P}_2 = \frac{\mathcal{P} - X_1\mathcal{P}_1^\circ}{X_2}$$

Debye used this method in his original study and found that $\mathcal{P}_2$ varied with concentration. This can be seen in Figure 9.

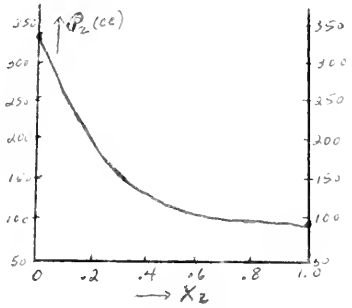


Figure 9. Polarization-Concentration Curve for Nitrobenzene

Even though $\mathcal{P}_2$ does change with concentration, such a graph can be used for determination of $\mathcal{P}_2$ at infinite dilution where X_2° = zero solute mole fraction. In this manner a value for $\mathcal{P}_2^\circ$ can be found in which the molecules are free from the

effects of intermolecular interactions.

Mathematically, this is represented by

$$\mathcal{P}_2^{\circ} = \lim_{X_2 \to 0} \frac{\mathcal{P} - X_1 \mathcal{P}_1^{\circ}}{X_2} \qquad (31)$$

Equation (30) then becomes

$$\begin{aligned} \mathcal{P}_2^{\circ} &= \frac{4\pi N}{3} \left(\frac{\mu^2}{3kT} + \alpha_v^{\circ} + \alpha_e^{\circ} \right) \\ &= \mathcal{P}_{2\mu}^{\circ} + \mathcal{P}_{2v}^{\circ} + \mathcal{P}_{2e}^{\circ} \end{aligned} \qquad (32)$$

where μ°, v°, and e° refer to the solute at infinite dilution in a given solvent.

In order to calculate μ from the known value of $\mathcal{P}_2^{\circ}$, the induction effect $(\mathcal{P}_{2v}^{\circ} + \mathcal{P}_{2e}^{\circ})$ must be separated from the orientation effect $\mathcal{P}_{2e}^{\circ}$ which contains the μ term. Graphical analysis of $\mathcal{P}_{2\mu}^{\circ}$ using a linear plot of $\mathcal{P}_2$ vs. 1/T is not effective in working with solutions, presumably due to the solute-solvent interactions which seem to be temperature dependent. According to Debye "departures from the linear relation connecting P and 1/T may be expected for lower temperatures or higher densities as soon as the mutual interaction of the molecules becomes of practical importance."[6]

For this reason a second method of measuring polarity is discussed in "Polar Molecules." Debye makes use of the well-known relationship of ϵ as a function of frequency. This frequency dependence is illustrated qualitatively in Figure 10. As the frequency increases in the region of

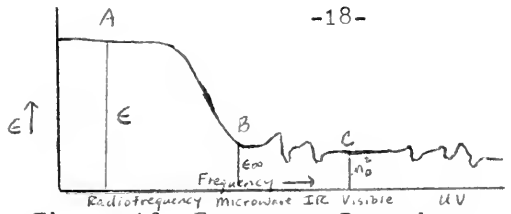


Figure 10. Frequency Dependance of ϵ.

B, the field is alternating so quickly that the orientation effect due to alignment of the permanent dipoles with the field no longer exists; there is not enough time for the dipoles to orient with the rapidly alternating field. Consequently

$$\mathcal{P} = \frac{\epsilon_\infty - 1}{\epsilon_\infty + 2}\frac{M}{\rho} = \frac{4\pi N}{3}(\alpha_v + \alpha_v) \qquad (33)$$

where ϵ_∞ is the dielectric constant in frequency range B. Similarly in region C only the components due to the induced shift in the electrons of the molecule remain. A similar shift is induced by the electric field of a light wave and results in the molar refraction equation

$$R = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{\rho} \qquad (34)$$

where R is the molar refraction and n the refractive index. This equation is obviously analogous to equation 18 and at the frequencies of region C

$$\epsilon = n^2 \qquad (35)$$

It has been found that the molar refraction for the yellow sodium D line (wavelength = 5893 Å) can be effectively used to determine $\mathcal{P}_e$.[7] Thus

$$\frac{n_D^2 - 1}{n_D^2 + 2}\frac{M}{\rho} = \frac{4\pi N}{3}\alpha_e = \mathcal{P}_e \qquad (36)$$

In solutions $\mathcal{P}_{1e}^{\circ}$ for the pure solvent can be used in place of $\mathcal{P}_{e}^{\circ}$, the value for the solution, as long as $\mathcal{P}_e \ll \mathcal{P}_\mu$. If this is not the case, refraction indices for solutions should be measured and extrapolated to infinite dilution as in equation (31).

The $\mathcal{P}_{zv}$ term is very difficult to calculate. In molecules where a reasonable value for the atomic polarizability has been determined, the value is "usually less than 15% of $\mathcal{P}_e$ and is sometimes no more than 3%."[8] Often a somewhat arbitrary value such as 5% $\mathcal{P}_e$ or 10% $\mathcal{P}_e$[9] is assigned to $\mathcal{P}_v$. In this study it seems reasonable to avoid such an arbitrary assignment by assuming that $\mathcal{P}_v = 0$. Since the value of $\mathcal{P}_v$ appears to be extremely small, no appreciable error will be introduced by this assumption unless the calculated moment is 1.0×10^{-18} D or less.

For the solution case, then, the Debye equation is

$$\frac{4\pi N}{3} \cdot \frac{\mu^2}{3kT} = \mathcal{P}_2^{\circ} - \mathcal{P}_{2v}^{\circ} - \mathcal{P}_{2e}^{\circ} = \mathcal{P}_2^{\circ}\mu \qquad (37)$$

$$\mu = 0.0128130 \times 10^{-18}\sqrt{\mathcal{P}_{2\mu}^{\circ} T} \qquad (37a)$$

In the numerical evaluation T is in degrees Kelvin, and the values for the constants are $N = 6.02252 \times 10^{23}$, molecules / mole, $k = 1.38054 \times 10^{-16}$ erg / molecule degree Kelvin, and $\pi = 3.14159$. The μ thus found, where $\mathcal{P}_2^{\circ}$ is evaluated from equation (31) and $\mathcal{P}_{2e}^{\circ}$ from equation (36), is expressed in Debye units.

VARIATIONS ON DEBYE THEORY:
Determination of Dipole Moment of Solutions

Although it is possible from the Debye equation to determine dipole moments as discussed above by extrapolating to $X_2 = 0$ and thus to infinite dilution, this procedure is not satisfactory due to the inherent error in the extrapolation. Two problems occur in this area: first, the extrapolation is not entirely accurate because of the curvilinear nature of the curves (see Figure 9); secondly, as the values for X_2 get smaller and smaller, the possibility for error increases tremendously.

Two of the methods of calculating dipole moments which attempt to eliminate these errors are the Hedestrand and the Halverstadt-Kumler methods. In the Hedestrand method[10] the assumption is made that the dielectric constant ϵ and the density ρ of the solution are linearly dependent upon the mole fraction of solute X_2 so that:

$$\begin{aligned} \epsilon &= \epsilon_1(1 + \alpha X_2) \\ \rho &= \rho_1(1 + \beta X_2) \end{aligned} \qquad (38)$$

Using the Clausius-Mosotti relation [equation (17)] and the Debye application to solutions, Hedestrand developed the following equation:

$$\mathcal{P}_2^{\circ} = A \cdot \left(M_2 - \beta\rho_1 \frac{M}{\rho_1}\right) + \beta\alpha\epsilon_1 \qquad (39)$$

where $A = \dfrac{\epsilon_1 - 1}{\epsilon_1 + 2} \cdot \dfrac{1}{\rho_1}$ $\qquad B = \dfrac{3M_1}{\rho_1(\epsilon_1 + 2)^2}$

The Hedestrand method can also be used if the solution is

expressed in terms of concentration, c (moles / liter) rather than in terms of mole fraction. In this instance

$$\epsilon = \epsilon_1(1 + \alpha' c)$$

$$\rho + \rho_1(1 + \beta' c)$$

and the equation for $\mathcal{P}_2^c$ becomes

$$\mathcal{P}_2^c = A(M_2 - 1000\beta'\rho_1) + C\alpha'\epsilon_1 \qquad (40)$$

where $\alpha' = \frac{M_1}{1000\epsilon_1} \cdot \alpha \quad \beta' = \frac{M_1}{1000\rho_1} \cdot \beta \quad C = \frac{3000}{(\epsilon_1 + 2)^2}$

The constants $\alpha\epsilon_1$ and $\beta\epsilon_1$ (or $\alpha'\epsilon_1$ and $\beta'\epsilon_1$ in terms of concentration can be easily evaluated by computing

$$\alpha\epsilon_1 = \frac{\epsilon - \epsilon_1}{X_2}$$

$$\beta\epsilon_1 = \frac{\rho - \rho_1}{X_2}$$

according to equation (38). For a more complete mathematical derivation, see Appendix IV.

A more recent variation in the Hedestrand method, first presented by Halverstadt and Kumler,[11] takes into account a possible solvent polarization error which is overlooked in the Hedestrand method. This is an error resulting "if it is not realized that the dielectric constant of the solvent in the solution sometimes differs considerably from the measured constant of the pure solvent."[11] Such an error can be due to the methods of handling, in which solutions are usually exposed longer to the air and consequently absorb more moisture than the solvent. Another component

of the solvent polarization error is due to the computation . ϵ_1, the solvent measurement is made only once, whereas ϵ for the solution is usually computed for different concentrations. The one value of ϵ_1 is weighted more heavily that the ϵ values (see equation 38).

Halverstadt and Kumler make a simple adjustment in the Hedestrand method to eliminate the solvent polarization error. They obtain values of $\alpha\epsilon_1$ and $\beta\epsilon_1$ by plotting X_2 vs. ϵ and X_2 vs. ρ respectively and using a least mean squares evaluation to obtain a straight line equation. The intercepts give the values of ϵ_1 and ρ_1 and the slopes are the values for $\alpha\epsilon_1$ and $\beta\epsilon_1$. The difference in the two methods lies in the fact that Hedestrand calculates the values for $\alpha\epsilon_1$ and $\beta\epsilon_1$ experimentally while Halverstadt and Kumler obtain these values by straight line plots.

This method of calculating Q_2^c is advantageous in that the extrapolations involve linear plots. The values of $\alpha\epsilon_1$ and $\beta\epsilon_1$ are calculated by extrapolation of the curves based on the solutions so that the ϵ_1 value obtained will not contain an error due to a difference between the measured value of ϵ_1 for the pure solvent and the actual value of ϵ_1 in the solution. If the solutions have absorbed water during their preparation, a discrepancy will be seen in the values of $\alpha\epsilon_1$ calculated in the Hedestrand manner as opposed to that obtained by the Halverstadt-Kumler method. If a contaminant

such as water, with a high dielectric constant, has been introduced, the $\mathcal{P}_2^{\circ}$ value will be too high, and the subsequent value for μ will also be too high.

One of the experimental problems in the Hedestrand and Halverstadt-Kumler methods is that the measurement of solution densities, a tedious chore, must be carried out with great accuracy. Guggenheim eliminates this problem in his method[12] but at the expense of requiring an equally accurate refractive index measurement.[13] According to the Guggenheim method, $\epsilon - n^2$ is plotted against the concentration c in moles / cc of the solution, and the slope is equal to

$$\frac{(\epsilon_1 + 2)(n_1^2 + 2)}{3} \cdot \frac{4\pi N}{3} \cdot \frac{\mu^2}{3kT} \qquad (41)$$

in which every quantity other than μ is known or can be measured. (A clear derivation can be found in the original article.)[12] The Guggenheim procedure seems to be quantitatively similar to the Halverstadt-Kumler method in that both methods yield approximately equivalent results. (Table 1)[13]. Which alternative is used must depend upon the equipment available and the accuracy possible in refractive index and density measurements.

Table 1 Electric moments of dibasic acids

Compound	Gugg.	H&K
Oxalic acid	2.66	2.71
Malonic acid	2.56	2.62
Succinic acid	2.08	2.11
Glutaric acid	2.47	2.50
Adipic acid	2.30	2.36

The above theories for determining dipole moments for dilute solutions are merely variations on the basic Debye theory as earlier discussed. These theories all depend upon the same assumptions concerning the internal field F acting upon a permanent dipole. Debye, using the Mosotti theory of the internal field, assumed that the field F is constant and can be obtained by taking the "time average of the field at a molecule due to all charges outside this molecule."[14] Onsager improves upon the Mosotti internal field theory by allowing for the relationship of the molecule to its environment.[15] According to Onsager, the internal field can be calculated as a function of θ, the orientation angle which the dipole moment makes with the field direction. When the environment of the polar molecule is considered, the local field theoretically can be found by holding the dipole at a constant angle θ and averaging over the thermal motions of the surrounding molecules, then repeating this procedure for all possible values of θ. It is important to note that in the Onsager theory the thermal motions of neighboring molecules are accounted for as well as the thermal motion of the reference molecule. Onsager also corrects for the fact that an isolated molecule will have a dipole moment which is slightly different from the apparent μ of a molecule immersed in a liquid.

The equation which Onsager developed, using his own definition of an internal field, is one in which the dipole moment can be obtained for pure polar liquids,

$$\frac{4\pi N}{3} \cdot \frac{\mu^2}{3kT} = \frac{(2\epsilon + \epsilon_\infty)(\epsilon + 2)}{3\epsilon(\epsilon_\infty + 2)} \cdot \left(\frac{\epsilon - 1}{\epsilon + 2} - \frac{\epsilon_\infty - 1}{\epsilon_\infty + 2}\right) \cdot \frac{M}{\rho} \quad (42)$$

$$= \frac{(\epsilon - n_D^2)(2\epsilon + n_D^2)}{\epsilon(n_D^2 + 2)^2} \cdot \frac{M}{\rho}$$

where n_D^2 is used as the value of ϵ_∞. Tests of this equation by comparing the values of μ with those obtained from measurements on μ of gases, indicate that it is accurate for pure polar liquids which do not show any abnormal interaction such as hydrogen bonding or complex formation.[33]

INSTRUMENTATION

In this project methods of obtaining dipole moments for solutions and for pure liquids are studied. In order to obtain experimental values for dipole moment according to the theory previously discussed, dielectric constants, refractive indices, and densities must be measured.

Measurement of Dielectric Constant

The measurement of dielectric constant is based on the effect of a dielectric material on the capacitance of an evacuated cell as given in equation (4), $C = \epsilon C_o$, where C_o is the capacitance of the evacuated cell. It is necessary to be able to measure the change in capacitance ΔC brought about by introducing a dielectric material between the plates of the capacitor. As discussed previously, the

value of ΔC is always positive; ϵ is by definition equal to 1 when the cell is evacuated and greater than one for a dielectric.

Two different circuits were constructed to measure ΔC, from which the dielectric constant can be calculated, a circuit involving the principle of resonance and a heterodyne beat circuit. The resonance circuit, first developed by Henriquez and modified by Alexander, is illustrated below as presented in Bender.[16]

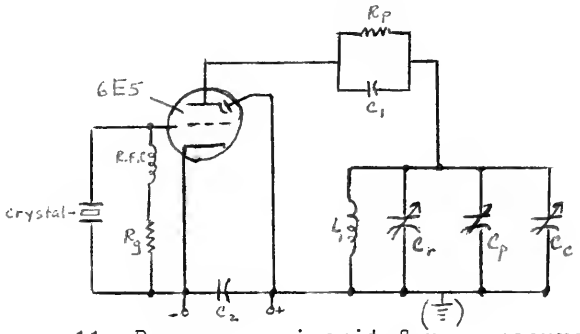


Figure 11. Resonance circuit for measurement

Resistors	Capacitors	Tubes, etc.
R_p ≐ 150,000 Ω	C_1 = .001 μf	6E5 tube
	C_2 = .01 μf	2.5 mh r.f.choke
R_g = 38,000 Ω	C_p = 11.5-160 μμf variable precision air capac.	2.604 meg crystal
		L_1 = 50 turns on 1" form with #26 wire
	C_r = 50 μμf coarse tuning capac.	
	C_c = dielectric constant cell	

250V was applied to the circuit from an external power source.

This method involves the use of a quartz crystal, which has a characteristic vibrational frequency, and an electron-ray tube, the 6E5 tube. The electron-ray tube serves simultaneously as an oscillator and a resonance detector.

The circuit pictured in Figure 11 essentially consists of two parts, the plate circuit and the grid circuit; it is known as a tuned-plate - tuned grid oscillator. The natural frequency of the grid circuit is constant due to the crystal, which will only vibrate at one frequency and offers a high impedance to alternating currents of different frequencies. Thus oscillation in the circuit can only take place if the frequency of the alternating current in the plate circuit is equal to that in the grid circuit. The grid and plate circuits are coupled (energy is transferred between the two) through the plate-grid capacitance in the tube. The plate and grid of the tube together act as a fixed capacitor. Alternating current of medium to high frequency can pass through easily, encountering little impedance, whereas this "capacitor" has a high impedance for direct current.

Because of the coupling in the 6E5 tube when in a tuned plate - tuned grid circuit, alternating current can pass freely between the plate and grid circuits. However, due to the presence of the crystal, this oscillation can only take place at the frequency of the crystal. The frequency

of the oscillation in the plate circuit thus determines whether or not oscillation will occur throughout the entire circuit.

When the condition of resonance is reached,

$$f = \frac{1}{2\pi\sqrt{LC}} \qquad (43)$$

where f is the frequency in cycles / second, L is the inductance in henries, and C is the capacitance in farads. Most resonance circuits have a relatively high impedance to frequencies other than the resonant frequency so that only the resonant frequency f is of interest in this discussion. If either L or C are changed, the resonant frequency will change. Since in the circuit described in Figure 11, the inductance is constant, a change in capacitance will control the resonant frequency in the plate circuit. Thus since the total capacitance of capacitors connected in parallel equals the sum of the individual capacitances, either the precision variable capacitor C_p or the coarse variable capacitor C_r can be adjusted, with a corresponding change in total capacitance, until oscillation occurs at the frequency of the crystal.

The electron ray tube in the circuit not only serves as an oscillator but as a detector. The target electrode, connected to the plate in this tube, is coated with a fluorescent material and is maintained at a potential positive

with respect to the cathode. Thus electrons flow from the cathode to the more positive target and produce a fluorescent glow when they strike the target. The flow of electrons to the target is controlled in the electron ray tube by a ray-control electrode. When this electrode is less positive than the target, electrons flowing towards the target are repelled and cannot pass beyond the control electrode to the target. In the area of the target which is not reached by electrons, no fluorescence is observed, and a shadow appears; characteristically this shadow is in the form of an angle which varies between 0° and 100° depending upon how negative the control is with respect to the target. (see Figure 12).

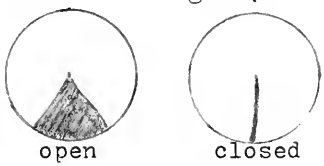


Figure 12.
Electron ray tube.

The full potential from the power supply is applied between the cathode and the target. When the circuit is not in oscillation, the potential of the plate and of the attached ray-control electrode will be less than that of the cathode because of the IR drop across the resistor R_p. The ray-control electrode will be negative with respect to the target and a large shadow area will appear. The angle will be 100° or "wide open."

The 6E5 electron ray tube is a triode tube. The grid

controls the flow of electrons from the cathode to the plate. When there is no oscillation in the circuit, the grid and the cathode are at practically the same potential. There is a current flow in the plate circuit which is limited only by the resistance of resistor R_p. As soon as oscillation begins in the circuit, the grid is exposed to an alternating current. During one half of the alternating cycle, the grid is positive with respect to the cathode and will attract electrons from it. Resistor R_g in the circuit, placed in the only path by which electrons can return to the cathode, increases the difficulty of return. A number of electrons are trapped on the grid in this manner and give it a negative bias with respect to the cathode. During most of the alternating cycle, the grid maintains a negative bias, and there will be little d.c. current between the cathode and the plate. In a portion of the cycle, however, the alternating potential on the grid is high enough to give the grid a more positive bias so that electron flow will take place from the cathode to the plate. Such a flow represents a d.c. current with a small alternating current component superimposed on it. The d.c. current produced in this manner is quite small, smaller than that which occurs when there is no oscillation.

The amount of d.c. current flowing in the circuit is

thus an indicator of whether or not oscillation has set in. If the capacitor in the plate tuning circuit is tuned from low capacity through the resonance point where oscillation sets in, a capacitance-current curve such as Figure 13 will be obtained.[16]

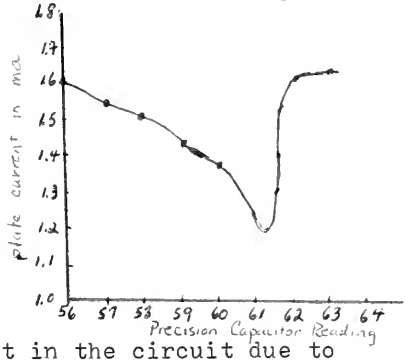


Figure 13. Variation in triode plate current as the plate tuning circuit LC is tuned through resonance

The reduction of current in the circuit due to oscillation causes a redistribution of the plate circuit potential. The effective resistance of the cathode to plate unit rises with a corresponding increase in the potential drop between the two. The potential of the ray-control electrode also rises with respect to the cathode, and it becomes less negative with respect to the target. The shadow angle will decrease until at the resonant point it is almost zero. When resonance has been passed, the shadow angle will suddenly widen out as oscillation in the circuit abruptly stops.

The actual measurement of dielectric constant using the resonance circuit is quite simple. The circuit is tuned to resonance with an empty cell, and then retuned to resonance when the cell is filled

with a dielectric material, the difference ΔC being read from the adjustment of the precision capacitor necessary to retune the circuit. It is important to note that after the first tuning to resonance with the empty cell, only the precision variable capacitor can be used to retune the circuit; otherwise an exact measure of the capacitance increment due to the dielectric would be impossible.

The heterodyne beat circuit, originally described by Chien[17] and reproduced by Smith,[18] is pictured schematically in Figure 14a[17] and in detail in Figure 14b.

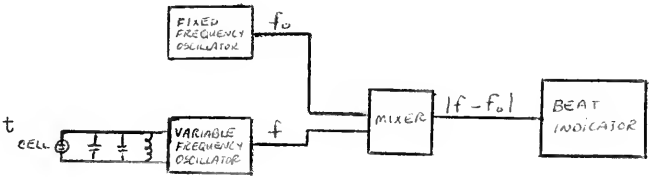
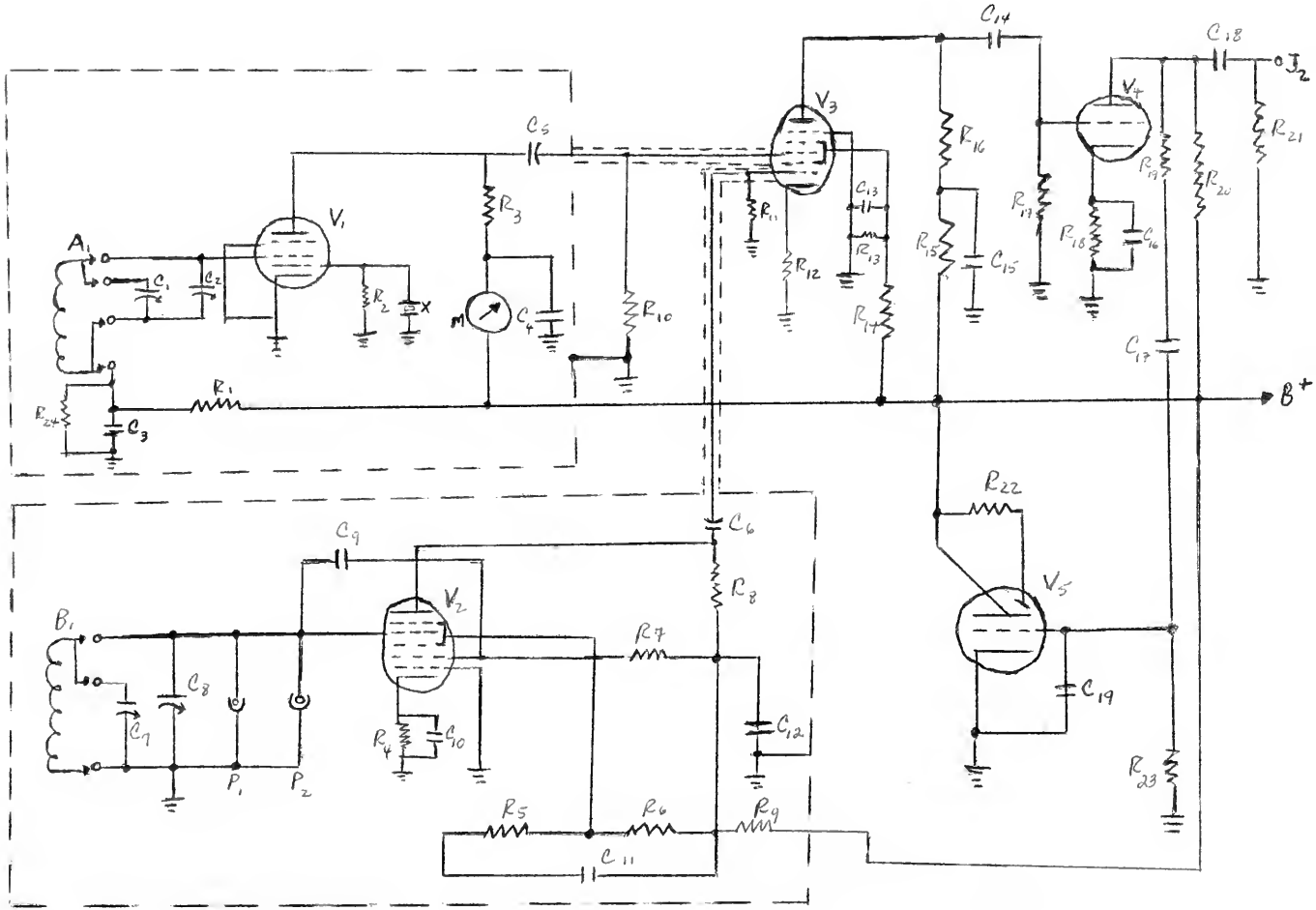


Figure 14a.
Schematic of
Heterodyne Beat
Circuit

Two radio frequency signals f_o and f are fed into a mixer so that the output is the difference between the two, $|f - f_o|$, or the beat frequency. The signal f_o is generated by a fixed frequency oscillator, f by a variable oscillator.

The fixed frequency oscillator is controlled by a quartz crystal in the circuit; as mentioned in the resonance section, the crystal will only vibrate at one frequency, characteristic of the structure and cut of the crystal. The ammeter in the circuit is used to indicate tuning of the oscillator. At full capacity the plate current is off scale. As the capacity is decreased by adjusting capacitor C_1, C_2, the current decreases to around 1.5 milliamperes,

FIGURE 14b. Heterodyne Beat Circuit



Specifics of Heterodyne Beat Circuit

Capacitors

C_1, C_2 = 200 μμf 4-gang variable
C_3, C_4, C_{13}, C_{18} = .1 μf 400 V
C_5, C_6 = 0-30 μμf air trimmer
C_7 = 650 μμf 4-gang variable
C_8 = 50 μμf variable
C_9 = 5100 μμf
C_{10}, C_{17} = .01 μf 400 volt
C_{11} = 10 μf 450 V
C_{12} = 2000 μμf
C_{14} = .25 μf 600 V
C_{15} = 4 μf 450 V electrolytic
C_{16} = 10 μf 150 V electrolytic
C_{19} = 300 μμf

Resistors

R_1 = 19600 ohm
R_2 = .47 megohm
R_{10}, R_{17}, R_{19} = .47 megohm
R_3, R_8 = 47,000 ohm
R_4 = 470 ohm
R_5 = 7000 ohm 1 watt
R_6, R_{13} = 15,000 ohm
R_7, R_{16} = 50,000 ohm (R_7 ¼ watt)
R_9 = 24,000 ohm 1 watt
R_{11} = .1 megohm ¼ watt
R_{12} = 154 ohm
R_{14} = 75,000 ohm 1 watt
R_{15} = 24,000 ohm
R_{18} = 2000 ohm
R_{20} = 51,100 ohm
R_{21} = o.5 megohm potentiometer
R_{22} = 1 megohm
R_{23} = 5.11 megohm
R_{24} = 31,600 ohm 1 watt

Note: All resistors are ½ watt unless otherwise specified.

Miscellaneous

V = 6SJ7
V = 6D8G
V = 6SA7
V = 6J5
V = 6E5
X = 2.00 meg. crystal
M = 0-5 ma. meter
(Heath Model EUW-18 Lab
Meter with 5 ma shunt)
J = oscilloscope lead
P = socket for coaxial wire connector to dielectric cell
P = socket for coaxial wire connector to external precision capacitor
(The precision capacitor was a variable air capacitor with a range of 11.5 - 160 μμf.)
Coil A = #26 wire wound to a length of 7/8 " on a 1 3/8 " form
Coil B = #26 wire wound to a length of 1 " on a 1 3/8 " form
Power Supply = Heath Model EUW-15 Universal Power Supply

at which point the oscillator is tuned to resonance, and oscillation has set in. If the capacity is further reduced, the current will again rise; at 3 ma the oscillator is tuned slightly off resonance and is in a position of maximum stability. The variable frequency oscillator, described by Chien as "an unusual type, but ... possessing stability and simplicity of construction,"[17] is constructed using a 6A8 type pentagrid converter tube. A detailed discussion of the electronic theory in this oscillator can be found in Chien.[17]

The two oscillators are fed into grids 1 and 3 of a 6SA7 mixer tube, which heterodynes the two signals, producing as an output the difference between the two, $|f - f_o|$. This beat frequency signal is then amplified by the 6J5 tube and fed into the grid circuit of the 6E5 tube, which acts as a detector. When there is no signal on the grid, the eye or shadow angle of the electron ray tube will be wide open; the plate current will be high, and the potential of both the plate and control electrode will be low due to the drop across R_{22}, a one megohm resistor. Upon receipt of a signal, the shadow angle decreases, as described in the resonance method section. When a large beat frequency is received by the 6E5 tube, the eye appears blurred. However, when the beat frequency decreases to a level below the persistence period of vision, a periodic blinking can be seen.

The beat frequency can also be detected by connecting a cathode ray oscilloscope to the output of the amplifier tube or by using earphones. When the beat frequency is small, it will be in the audible range, frequencies of 15 to 15000 cps. The earphones are advantageous in that it is easy to tell by the pitch of the sound whether the capacitance change results in a movement away from or towards the zero beat point.

Regardless of the method of detection, the dielectric constant is measured using the heterodyne beat method by setting zero beat as a reference point with the empty cell; the cell is then filled with a dielectric material, and the zero beat is found again, the value for ΔC being the necessary adjustment of the precision capacitor.

One of the main advantages of this particular heterodyne beat circuit is that the phenomenon of "locking-in", usually seen in circuits of this nature, is avoided. When f and f_o are nearly equal, usually the more stable oscillator exerts a synchronizing effect over the less stable one so that the two oscillators in this range will be locked in step or at the same frequency. A sharp zero beat setting cannot be observed, and thus the accuracy of the measurement is seriously reduced. In this circuit, however, beat frequencies down to one beat per second can be observed.[17]

EXPERIMENTAL AND RESULTS

The experimental section is devoted to discussion regarding

the actual implementation of resonance and heterodyne beat circuits as well as to the methods of measurement of density and refractive index.

An instrument was constructed which consists of both the heterodyne beat and resonance circuits, connected by a common precision capacitor. A switch is provided so that the precision capacitor can be switched easily from one circuit to the other. Details of the circuitry including values of the resistors, capacitors, and inductors involved can be seen in Figures 11 and 14b.

Construction of the resonance circuit was relatively easy. The only major problem which occurred was that of the ground connection in the LC unit of the plate circuit (enclosed in parentheses in Figure 11). In looking at the schematic of the circuit (Figure 11), there seems to be a direct short from the positive connection to the grounded side of the LC unit. The instrument which I constructed omits this lead and is functional. After correspondence with Dr. Paul Bender,[19] author of one of the original articles suggesting this circuitry[16], it is obvious that the problem lies within the power supply rather than in the resonance circuit itself. Dr. Bender pointed out that the ground connection in the resonance circuit LC unit is a positive ground. The circuit described can be used only with a modified power supply in

which the negative side is not grounded; otherwise a direct power supply short will result. The power source used in this study is a Heath Model EUW-15 Universal Power Supply wired as a voltage doubler rectifier. The negative side of this supply is grounded, with the -d.c. lead running to the center tap of the power transformer, which is grounded to the chassis. Thus the LC ground lead must be omitted in the resonance circuit described by Bender when using this type of power source. As Dr. Bender notes, however, when a normal power supply is used and the ground lead in the LC unit omitted, a shock hazard exists due to the fact that the LC unit is at a positive potential. Care must be taken when working with the circuit as it is now set up.

The heterodyne beat circuit, necessarily more complicated than the resonance circuit, presented a greater problem in implementation. It is important to note (and easy to overlook in the circuit diagram) that both the variable and fixed frequency oscillators as well as their leads into the mixer tube must be carefully shielded . The purpose of this shielding is to prevent stray radio frequency signals within the circuit. Such stray signals can be picked up by the sensitive detector and will interfere with the location of the zero beat reference point. In my instrument adequate shielding is provided by enclosing the circuits in grounded aluminum

chassis units. All connections from these boxes to the cell and to the chassis containing mixer, amplifier, and detector tubes are made with coaxial cable. The leads from the outer surface of the mixer chassis to grids 1 and 3 of the mixer tube are sub-miniature coaxial cables so that both the fixed and the variable oscillator signals are shielded up until the point at which they enter the mixer tube.

Since both the resonance and heterodyne beat circuits are designed to measure a change in capacitance, one of the largest problems is that of stray capacitance. A capacitor consists of two metal plates separated by a specific distance. It is easy to see that any two wires in a circuit can act as a capacitor and thus contribute to the stray capacitance. For this reason all leads within both circuits were kept as short as possible. The use of coaxial cable, which consists of an inner wire, used to carry the signal, surrounded by an outer sheath of grounded wire used to shield the signal, can also introduce stray capacitance, with the inner and outer wires acting as a capacitor. The stray capacitance introduced by the coaxial cable in the heterodyne beat circuit, however, is negligible and is certainly not great enough to outweigh the shielding of the radiofrequency signals.

Several sources recommend construction of a dielectric constant cell by using a variable capacitor of around 50 $\mu\mu f$ which has had several of the plates removed.[34, 20] It was found, however, that it is unnecessary to build a cell for ordinary measurement. Instead a conductivity cell designed to contain can be used. The conductivity cell has platinum plates separated by approximately 1.5 cm., with only 7-8 ml. of the dielectric material required to completely cover them. Both plates are connected to mercury "leads" which are then connected in parallel by platinum wires to the precision capacitor (see Figure 15). Disadvantages of this arrangement result mainly from the possibilities of stray capacitance

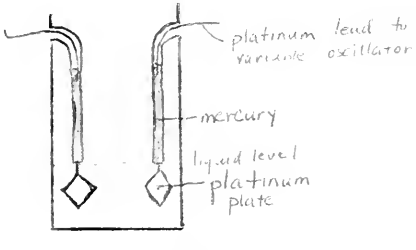


Figure 15. A conductivity cell used as a dielectric constant cell.

and inductance; the platinum leads are separated by approximately 3 cm. at the points of their exit from the cell, and they can thus act as a capacitor. Another problem with this type of cell is that it cannot be placed in a fixed position. It must be emptied from the top after every measurement and must therefore be movable. It is difficult to return the

cell to the exact same position after each measurement, and the lead capacitance from the cell will be slightly different for each reading. For normal use the advantages of having a readily available, relatively inexpensive cell which has a low capacitance when empty (on the order of 7 $\mu\mu F$), seem to outweigh these disadvantages.

The construction of the heterodyne beat circuit, because of its complexity, is time-consuming but can be done by an amateur with the help of sources like the Radio Amateur's Handbook.[21] Troubleshooting the finished product presents an even greater problem and calls for a knowledge of electronics, as well as familiarity with the particular circuit involved. For this reason I have prepared a troubleshooting chart as well as a set of instructions for operation based on my experiences with the Chien heterodyne circuit. These are given in Appendices V and VI.

The actual method of detection of zero beat in my circuit is a Techtronix 515A oscilloscope. It is important to note that the scope used must be able to chart the flow of electrons in both radio and intermediate frequency ranges to be useful as a tuning device. Through the use of the Techtronix 515A scope, it is possible to heterodyne the variable and fixed signals to approximately zero beat, which appears as a solid band on the screen (Figure 16).

When the circuit is not adjusted to zero beat, the beat frequency can be read by calculating the frequency of the signal appearing on the scope. As the capacitance in the variable frequency oscillator circuit is adjusted, the sinusoidal curve on the scope (tracing the beat frequency) gradually becomes more extended due to decreasing beat frequency. On the other side of the solid band indicating zero beat, the sinusoidal curves reappear. (Figures 16-20).

In the circuit which I constructed the electron ray tube does not seem to be effective as a detector. A blur can be seen in the eye when the circuit is not at zero beat, but the periodic blinking described by Chien[17] near zero beat is not present. This is probably due to the fact that with the precision capacitor used in the present circuit, the smallest capacitance increments which can be added are so large that the beat frequency passes from beyond the persistence period of vision to very near the zero beat point.

The accuracy of the heterodyne beat circuit depends upon how reproducible the zero beat setting is and upon the accuracy of the calibration of the precision capacitor. In my instrument the zero beat setting is accompanied by a "dead-band" in the capacitor; there is a range of capacitance settings at which the oscilloscope shows continually a zero beat. The dead-band range varies depending upon whether

Figure 16. 2.6 meg. signal from fixed frequency oscillator Scale = .5 microsec / cm.

Figure 17. Band indicating zero beat Scale = .5 millisec / cm.

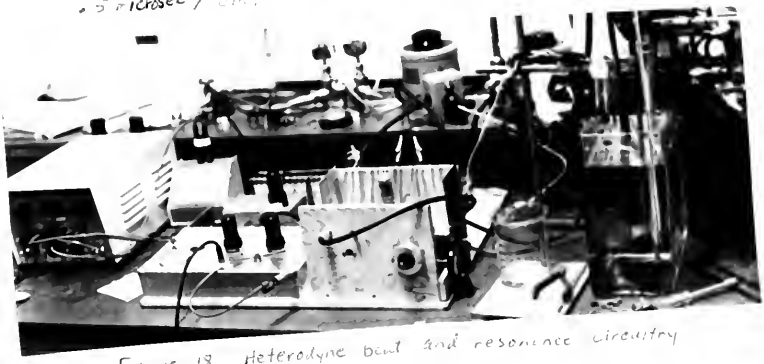


Figure 18. Heterodyne beat and resonance circuitry

Figure 19. Beat frequency near zero beat
Scale = .1 millisec / cm

Figure 20. Beat frequency
Opposite [illegible]
beat from [illegible]
Scale = [illegible] millisec / cm

or not the capacitor is more nearly closed or open. When the capacitor is almost closed, the dead-band decreases. This decrease in the dead-band in the areas of higher capacitance is probably due to the nature of a variable capacitor. When it is full open, a slight turn will mesh the plates only slightly, with a small increase in capacitance. When the capacitor is more fully closed, however, the plates are almost completely meshed and the resulting capacitance change for a slight adjustment will be higher. In any case, the average of the maximum and minimum readings of the dead-band region is taken to be the value of the zero beat frequency. Examples of the dead-band can be seen in Table 2.

Table 2 Selected dead-band readings on the precision capacitor

Reading #	% Capacitor is closed (approximate)	Absolute readings at 0 beat	Dead-band
1	12	23.900 - 23.600	.300
2	43	22.320 - 22.286	.130
3	68	15.465 - 15.354	.111
4	80	9.574 - 9.522	.052
5	88	5.358 - 5.340	.018

Note: Absolute readings decrease as the capacitor is closed. The first significant figure in readings #1,2, and 3 was not actually read on the vernier, but is used to distinguish between complete rotations as will be explained later.

There is a plausible explanation for the dead-band region: the circuit which I constructed using the

Techtronix 515A scope as a detector is incapable of measuring the extremely small capacitance increments which are added over the region of the deadband. In this case, the total capacitance increment over the region of the dead-band would be the smallest increment which affects the signal on the oscilloscope. The precision capacitor used covers a range of 11.5-160 $\mu\mu f$ from fully open to fully closed. It takes approximately 6 complete rotations of the ten-turn vernier dial (i.e. 60 turns) to measure the full range of the capacitor. This indicates that one turn (consisting of 1000 divisions) is equivalent to around 2.48 $\mu\mu f$ with 1 division being approximately .00248 $\mu\mu f$ (assuming that the capacitance is linear). A dead-band of 25 divisions (corresponding to a difference in the two readings of .025) will thus be equivalent to approximately .062 $\mu\mu f$ or .04% of the total capacitance. Such a dead-band limits the accuracy of the measurement to the third significant figure. If dielectrics are measured which have small dielectric constants, such as benzene, the error due to the dead-band will be greatly magnified. An attempt to solve the problem by using a less sensitive vernier dial will result only in disguising rather than eliminating the dead-band. A change in circuitry is necessary to decrease or altogether eradicate the problem.

Calibration of the precision capacitor is another important factor in the accuracy of both the resonance and heterodyne beat methods. The ideal way to calibrate the capacitor is to use another previously calibrated precision capacitor. Since such a capacitor is expensive and currently unavailable at Sweet Briar College, an alternative method was attempted. A 4.254 $\mu\mu f$ fixed capacitor was used as well as a blank banana plug. Because the capacitor covers such a large range (11.5 - 160 $\mu\mu f$), it was found that it was unnecessary to calibrate the entire capacitor. Instead only 1 complete rotation, or 10 turns of the vernier dial, was calibrated, in the region in which the capacitor is nearly closed (at about 75% of the total capacitance). This region was chosen because in this area the dead-band is fairly small. For convenience another dial is on the capacitor, divided into 100 divisions over the range of the entire capacitor. The region in which the capacitor has been calibrated corresponds to 78.8 - 58.9. (Due to the gear mechanism in the precision capacitor, as the precision vernier reading increases, the coarse vernier reading decreases. An increase in the precision vernier and a decrease in the coarse vernier correspond to a decrease in the total capacitance; the capacitor is more open).

The actual mechanics of the attempted calibration are as follows:

1) The coarse capacitor is adjusted so that with the precision capacitor set at 0.000 on the vernier and 78.8 on the reference dial, a zero beat frequency is obtained. At this time a blank banana plug is connected to the precision capacitor leads. (The cell is <u>not</u> used in the calibration).

2) The blank is replaced by the 4.254 $\mu\mu f$ capacitor, and the precision capacitor is then adjusted to give a zero beat frequency. The ΔC between the original zero beat setting and the new one is recorded. Note that the precision capacitor reading must decrease to compensate for the addition to the circuit of the 4.254 $\mu\mu F$ capacitor.

3) The 4.254 $\mu\mu F$ capacitor is removed and the blank reinserted. The <u>coarse</u> capacitor is then adjusted to give a zero beat frequency.

4) Steps 2 and 3 are repeated over the desired calibration range of the precision capacitor.

The calibration of the precision capacitor in this manner enables a calculation of the Δcapacitance per unit or division for each 4.254 $\mu\mu f$ addition. The following results were obtained:

<u>Table 2</u> Calibration of the precision capacitor using a 4.254 $\mu\mu f$ capacitor

Reading	Δ reading /4.254 $\mu\mu f$	$\mu\mu F$/division
0.742	0.742	.005733
1.636	0.894	.004758
2.544	0.908	.004685
3.508	0.964	.004412
4.511	1.003	.004241
5.570	1.059	.004016
6.710	1.130	.003764
7.920	1.210	.003515
9.255	1.335	.003686

Assuming that the calibration of the precision capacitor was accurate, I used these results in the calculation of the cell constant C_o. The capacitance value for C_o represents the capacitance of the cell when it is evacuated. In order to find C_o, the following relations were used:

$$C_2 = \epsilon C_o + C_L \qquad (44)$$

$$C_1 = C_o + C_L \qquad (45)$$

The C_L value stands for lead capacitance and any additional capacitance due to circuitry. If equation (45) is subtracted from equation (44), then

$$C_2 - C_1 = \epsilon C_o - C_o$$
$$\Delta C = (\epsilon - 1)\ (C_o)$$

Note that in measuring a change in capacitance, the lead capacitance term cancels out. Thus the problem mentioned earlier concerning the movement of the cell and subsequent differences in lead capacitance is eliminated.

The circuit is brought to zero beat by adjusting the coarse capacitor when the precision capacitor reads 0.000. It follows that the actual reading on the vernier dial after the dielectric is added and the instrument is readjusted to zero is equivalent to the change in capacitance.

In the determination of the cell constant C_o, 4 organic compounds were used, benzene, nitrobenzene, n-butanol, and iso-propanol. 10-12 ml. of each was fractionally distilled

on a Nester-Faust spinning band distillation column which has on the order of 2000 theoretical plates. The distillate in each distillation was taken off at the rate of 1 drop / 5 drops in reflux. The fractions used represent the fractions nearest the boiling point (allowing for thermometer calibration errors) in a 2° range.

Table 4 Fractional distillation data

Organic compound	Grade	B.P. of fraction removed °C	B.P.[21a] °C
Benzene	Fisher Cert. A.C.S.	78.0 - 78.1	78.11
Iso-propanol	'Baker Analyzed' Reagent	79.0 - 80.8	
N-butanol	Mallinckrodt Anal. Reagent	113.8 - 115	117.5
Nitrobenzene	'Baker Analyzed' Reagent	205 - 206	210.8

The distillation was carried out at a pressure of approximately 1 atm.

All readings were taken when the cell was in a constant temperature bath of 25°C. A mineral oil bath of low dielectric constant was used in place of water, which has a high dielectic constant, and could introduce another error in the reading. The cell was filled to the same level with each dielectric so that the plates were fully covered. The depth of immersion in the bath was kept constant. In addition, dielectric substances were placed in the bath at least thirty minutes before measurement to assure that their temperature was that of the bath. Results of the calibration are given in Table 5.

Table 5 Determination of the cell constant using the 4.254 $\mu\mu f$ fixed capacitor

Organic Compound	Δ reading	ΔC	Error Due to Dead-band	Cell Constant
Benzene	0.085 ± .005	.4385	6%	.3445
N-butanol	0.702 ± .002	3.522	.3%	.2188
Iso-propanol	0.738 ± .012	3.697	2%	.2137
Nitrobenzene	1.395 ± .035	6.797	3%	.2002

An obvious error, presumably in the method of calibration, can be seen in the fact that the cell 'constant', using the calibration method described previously, is not found to be constant. Another variation of this particular calibration was used, in an effort to correct for the problem. Assuming that for each 4.254 $\mu\mu f$ range the capacitance was linear, the total change in capacitance was determined by an extrapolation procedure. The change in reading due to the presence of each organic compound as dielectric was divided into the change in reading for each 4.254 $\mu\mu f$ addition in the calibration, this fraction being then multiplied by 4.254. In the case of nitrobenzene, the process was slightly different because the change produced by the dielectric was greater than the change produced by one 4.254 $\mu\mu f$ increment. For nitrobenzene 4.254 was added to the product $\frac{.653}{.894} \cdot 4.254$ to obtain the ΔC for nitrobenzene. In recomputing the cell constant the same reading for each chemical was used so that only the method of calculation of the cell constant differed. The C values obtained in this manner can be seen

in Table 6.

Table 6 Calculation of the cell constant using an extrapolation method

Compound	C	Cell Constant
Benzene	.4873	.3837
N-butanol	4.025	.2500
Iso-propanol	4.231	.2446
Nitrobenzene	7.361	.2177

Again the C_o value was not constant, leading me to believe that there was some inherent error in the calibration. The obvious error in the calibration is that the instrument is not accurate to the fourth place so that it is impossible to readjust to the zero point by adding exactly 4.254 $\mu\mu f$. Instead, approximately 4.25 $\mu\mu f$ were being added; in the calculation of the cell constant, this lack of accuracy in the calibration can lead to erroneous values for C_o. Another contributing factor to the calibration error is that the zero point readjustment was made each time by the coarse variable capacitor. (See step 3 in the calibration description). The coarse capacitor is not capable of slight capacitance adjustments or extreme accuracy.

Thus in the analysis of the cell constant, it seemed reasonable to me that the error was in the calibration procedure rather than in the readings for the different chemicals, which were reproducible and had errors of from .2% to 6% due to the dead-band, not enough to cause such a variation in the cell constant. Another calibration procedure was therefore attempted. This time the known values

for the dielectric constants of the different organic compounds were used as calibration standards. It was assumed that the precision capacitor was linear in the range which was being calibrated. This is a reasonable assumption since such a small range was calibrated. The actual reading from the precision capacitor was plotted against $\epsilon - 1$ according to the relationship

$$\Delta \text{ reading} = (\epsilon - 1)(C_o)$$

The value for C_o was obtained by a least mean squares analysis for the four compounds. The results are as follows:

Table 7 Calculation of C using known values of[22]

Compound	Δ reading	$\epsilon - 1$	C_o
Benzene	.085	1.27	.06693
N-butanol	.702	16.1	.04360
Iso-propanol	.738	17.3	.04208
Nitrobenzene	1.395	33.82	.04124

Since the benzene reading contained an error of 6%, and since the dielectric constant and subsequent capacitance change for benzene is so small, the value of C_o, which is statistically insignificant in a linear plot, is disregarded. The cell constant value obtained when disregarding the benzene value and analyzing the data by the least mean squares method is .03939 and can be used, in conjunction with the reading to determine values of $\epsilon - 1$ for unknown dielectric materials, from which ϵ can be readily figured.

When considering the accuracy of the instrument, the

[illegible]

Δ reading values must be studied. With the precision capacitor in the circuit, a dielectric such as nitrobenzene, with a high dielectric constant, gives a Δreading of only 1.395, which is quite small when considering the size of the capacitor. As mentioned previously the importance of the error due to the deadband is magnified when the Δreading is small. It is possible to increase the Δreading by removing some of the plates in the precision capacitor so that 1 turn will correspond to fewer $\mu\mu F$. Another possibility is to use a different precision capacitor, preferably a smaller one, which has a gear mechanism so that there are fewer $\mu\mu F$ / turn. For an accuracy of 2-3%, the instrument is limited to measurement of dielectrics with a high dielectric constant unless one of the above adjustments is made. For work on solutions and on pure material of low dielectric, a change in the precision capacitor is recommended.

Measurement of Density and Refractive Index

Determination of dipole moment from the equations given by Debye,[1] Halverstadt and Kumler,[11] and Onsager[15] requires both density and refractive index measurements. Although it is possible for pure liquids to use handbook values for density, when solutions are used for dipole moment determination, measurement of the density of the solution must be performed experimentally. A detailed discussion of density measurement can be found in Weissberger.[23] In this

project a pycnometer was used to determine the densities of 4 reagent grade chemicals. First the exact volume of the pycnometer was obtained in the following manner:

1) The pycnometer was carefully washed and dried in an oven. It was placed in a dessicator until it returned to room temperature, at which time it was weighed on a Mettler balance.

2) The pycnometer was filled with distilled water which had been boiled within the last two hours for removal of CO_2 and other gases. The capillary stopper in the pycnometer insured that a reproducible liquid level could be obtained. Any excess liquid on the outer surface of the pycnometer was carefully removed with filter paper. The pycnometer was always handled after drying with chem-wipes to prevent an additional weight due to hand moisture. The weight of the pycnometer when filled with water was recorded using the Mettler balance.

3) The temperature at which the measurements were taken was recorded.

4) Steps 1, 2, and 3 were repeated until constant readings (with differences of less than 1 part / thousand) were obtained.

5) The volume of the pycnometer was calculated by using the known value for the density at the particular T at which the water was weighed.

Using the calculated volume of the pycnometer, 25.9813 ml., the densities of 4 reagent grade chemicals were determined and compared with known values. This was done to test the accuracy of the method used. Results are given in Table 8.

Table 8 Density calculations

Comp. #	Compound	Wt. in ml.	Exp. Dens. g/ml.	Actual Dens.[21] g/ml.
(1)	2,2,4-Trimethylpentane	17.8378	.6866	.6918
(2)	2-methyl-2-butanol	20.9828	.8076	.8048
(3)	3-methyl-1-butanol	20.9361	.8058	.8092
(4)	Cyclopropanone	24.5669	.9455	.9978

From these results a computerized calibration "curve" was made using the method of least mean squares. The slope of the linear plot obtained when plotting the actual density on the X axis vs. the experimental density on the Y axis is .828223 and the Y intercept is .12376. The actual curve fit is seen in Table 8a.

Table 8a Curve fit of density values

Comp #	Actual Density g/ml.	Exp. Density g/ml.	Density for LMS fit g/ml.	% Differ
(1)	.6918	.6866	.7003	1.9
(2)	.8048	.8076	.7939	-1.6
(3)	.8092	.8058	.7976	-1.0
(4)	.9978	.9455	.9538	.8

Refractive index measurements for the pure liquid can also be obtained from the handbook. However, an adjustment must be made for temperature changes. Corrections can be made according to the known relationship that for each °C rise from the temperature at which the stated value of the refraction index is given, the index decreases .0004.

The Guggenheim method for measurement of dipole moments is solution requires an exact measurement of the refractive index of the solution. Such a measurement can be performed at Sweet Briar using a Spencer Abbe-type refractometer. To test the accuracy of the instrument, the refractive indices of 4 pure organic chemicals were measured using a sodium lamp as the light source. After temperature adjustments the results were compared with

handbook values. A calibration "curve" similar to the density plot was again made. The Abbe refractometer was found to give highly reproducible results which are accurate.

Table 9 Refractive index values

Compound	n_D (Hand.Value)	n_D Exp.	n_D in plot	%Differ.
Benzene	1.3747	1.3761	1.3755	0
N-butanol	1.5506	1.5493	1.5485	0
Iso-propanol	1.4991	1.4968	1.4979	0
Nitrobenzene	1.3972	1.3973	1.3976	0

Handbook values are corrected to a temperature of 25 C.

In view of the added difficulty of density determination in the Halverstadt-Kumler method for solution, the Guggenheim method seems more useful at Sweet Briar since accurate measurements of n_D can be made.

APPLICATIONS

Dipole moment measurements were originally a primary source of information about the structure of molecules. Debye, for example, based his postulates concerning the OH bond angle in water on the fact that H_2O exhibits a net dipole moment.[24] Today, however, sophisticated spectroscopic and diffraction techniques have superseded dipole moment measurements in the determination of molecular structure, especially for smaller molecules. The usefulness of dipole moments currently lies in studying conformational equilibrium in molecules exhibiting some degree of free rotation. Our knowledge of bond angles, bond lengths, and bond moments in most molecules is sophisticated enough so that a reasonably accurate prediction of the

moment for various geometrical isomers can be determined.[25] These values can be compared with the experimental values to obtain a knowledge of rotational hindrances, the effect of temperature on rotation, etc. Dipole moments are also useful in certain mechanism studies in which evidence for stereospecific addition exists or in which the product is formed by a ring opening.

The generalized applications discussed above require accurate theoretical predictions of the dipole moments of the molecules being studied. A detailed analysis of the mathematical calculations involved is beyond the scope of this paper. Excellent references on this subject can be found in references 26 and 27,[26,27] with specific examples given in references 28,29, and 30.[28-30] Possible projects are mentioned below.

1. Development of a student experiment involving the investigation of the addition of bromine to the double bond in cyclohexene to determine whether addition is -cis or -trans.

2. Investigation of the accuracy of the Wilcox method[28] of predicting the dipole moments of derivatives of bicyclo- 2,2,1 -heptane, bicyclo- 2,2,1 -hexane, and bicyclo- 1,1,1 -pentane. Wilcox has prepared in tabular form the coordinates in the x,y, and z planes of the various carbons in these molecules as well as the unit vectors radiating out from the carbons in the direction of the substituents or the hydrogens. Quick calculations from these tables should lead to a good theoretical prediction of the dipole moments

An interesting study in light of this article could be made on 5-norbornene-2,3-dicarboxylic acid.

3. Investigation of the mechanism of ring opening in strained molecules. Study of dipole moments of the products would indicate whether the ring opening is conrotatory, disrotatory, or a combination of the two.

4. Further investigation of cis-trans equilibria in molecules where such an equilibrium is thought to exist.[31] Dipole moments of both the cis- and trans- isomers are predicted and compared with the experimental value, which will presumably be intermediate between the two values for cis- and trans-.

5. Further investigation of Onsager's theory as applied to solutions of polar solutes in non-polar solvents.[15,31]

6 Further investigation of association in solutions through an application of the Onsager theory of determining dipole moments for pure liquids. The dipole moment obtained for a dilute solution in a non-polar solvent could be compared to that for the pure liquid to determine the degree of association. If a great deal of association occurs, the dipole moment will differ considerably from that predicted by the measurement for the pure liquid.

CONCLUSION

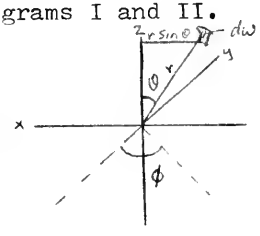
This project has primarily been concerned with setting up the instruments and equipment necessary for the determination of dipole moments. It is hoped that investigations involving dipole moment theory can be carried out in the future at Sweet Briar using the now available dielectric-constant "meter" , the calibrated pycnometer, and the Spencer Abbe-type refractometer.

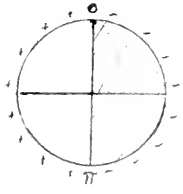
Appendix I
Derivation of F[1]

$$\int_{surface} = \frac{P\cos\theta}{r^2}\, d\omega \qquad (1)$$

The value for equation (1) can be obtained by considering diagrams I and II.

I





$d\omega$, a small segment of the surface area of the sphere generated by rotating r and $r\sin\theta$ equals $r\, d\theta \cdot r \sin\theta\, d\phi$ which when integrated over ϕ yields

$$d\omega = \int_0^{2\pi} r\, d\theta\, r \sin\theta\, d\phi = 2\pi r^2 \sin\theta\, d\theta \qquad (2)$$

If the sphere is in a dielectric, the effect of the field on the boundary between the dielectric and the sphere will be equal for the two halves. (Diagram II) Thus it is necessary to consider only $\frac{1}{2}$ of the sphere. Since the F term is derived by considering the forces on each individual surface element, the actual force F is a resultant, and an additional $\cos\theta$ term is introduced into equation (1). Substituting (2) into (1), and allowing for the additional $\cos\theta$,

$$\int_{surface} = \int_0^{\pi} \frac{P\cos^2\theta}{r^2} \cdot 2\pi r^2 \sin\theta\, d\theta = \frac{4\pi P}{3}$$

Appendix II
Mathematics of the Clausius-Mosotti Derivation[4]

According to equation (16) $P = n\alpha(E + \frac{4\pi P}{3}$ and from equation (8) $D \equiv E + 4\pi P$.

$$\frac{D-E}{4\pi} = P = n\alpha\left(E + \left[\frac{4\pi}{3}\left\{\frac{D-E}{4\pi}\right\}\right]\right)$$

$$\frac{\epsilon E - E}{4\pi} = n\alpha\left(E + \frac{D-E}{3}\right)$$

$$\frac{E(\epsilon-1)}{4\pi} = n\alpha\left(\frac{3E + D - E}{3}\right)$$

$$\frac{E(\epsilon-1)}{4\pi} = \frac{n\alpha 2E}{3} + \frac{Dn\alpha}{3}$$

$$\epsilon - 1 = \left(\frac{4\pi n\alpha 2E}{3} + \frac{4\pi Dn\alpha}{3}\right) \times \frac{1}{E}$$

$$= \frac{4\pi n\alpha}{3}\left(2 + \frac{D}{E}\right)$$

$$\frac{\epsilon-1}{\epsilon+2} = \frac{4\pi n\alpha}{3}$$

Appendix III

Derivation of Equation (22) $\bar{m} = \frac{\mu^2}{3kT} F$ [1]

$$\bar{m} = \frac{\int_0^{4\pi} A e^{(\mu F/KT)\cos\theta} \mu \cos\theta \, d\omega}{\int_0^{4\pi} A e^{(\mu F/KT)\cos\theta} d\omega}$$

Let $\frac{\mu F}{KT} = x$, $\cos\theta = y$; by definition $d\omega = 2\pi \sin\theta \, d\theta = 2\pi \, dy$

$$\frac{\bar{m}}{\mu} = \frac{\int_{-1}^{+1} e^{xy} y \, dy}{\int_{-1}^{+1} e^{xy} dy}$$

Since $\int_{-1}^{+1} e^{xy} dy = \frac{(e^{x} - e^{-x})}{x}$

$$\frac{\bar{m}}{\mu} = \frac{e^{x} + e^{-x}}{e^{x} - e^{-x}} - \frac{1}{x} = \coth x - \frac{1}{x} \equiv L(x)$$

Here coth x means the hyperbolic cotangent of x, and L(x) represents the Langevin function. This derivation is given the name of Langevin due to the fact that it resembles Langevin's calculation of the mean magnetic moment of gas molecules with a permanent magnetic moment.

When L(x) is expressed in a power series,

$$\coth x = \frac{1}{x} + \frac{x}{3} - \frac{x^3}{45} + \ldots$$

$$\coth x - \frac{1}{x} = \frac{x}{3} - \frac{x^3}{45} + \ldots$$

In most cases all but the first term can be neglected.

Appendix III (cont.

$x = \frac{\mu F}{kT}$ is a small fraction (considering a capacitor with plates separated by 1 cm. and charged to 3000 V, $F = 10^{-18}$ and $kT = 10^{-14}$ erg at room temperature)[36] and thus will not affect appreciably the value of $L(x)$. Since $x \ll 1$, $L(x) = \frac{x}{3}$, its first approximation, is thus used in this derivation.

$$L(x) = \frac{x}{3}$$

$$m = \frac{\mu F}{3kT} \cdot \mu = \frac{\mu^2 F}{3kT}$$

Appendix IV
Calculations for Hedestrand[10] Method

$$\mathcal{P} = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{\rho} \qquad (1)$$

$$\mathcal{P}_{solution} = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{X_1 M_1 + X_2 M_2}{\rho} = X_1 P_1 + X_2 P_2 \qquad (2)$$

$$\mathcal{P}_2 = \frac{\mathcal{P} - X_1 \mathcal{P}_1}{X_2} \qquad (3)$$

Given (1), (2), and (3) and substituting (2) into (3)

$$\mathcal{P}_2 = \frac{\left(\frac{\epsilon - 1}{\epsilon + 2}\right)\left(\frac{X_1 M_1 + X_2 M_2}{\rho}\right) - X_1 P_1}{X_2}$$

$$= \frac{\frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{X_2 M_2}{\rho} + \frac{\epsilon - 1}{\epsilon + 2} \frac{X_1 M_1}{\rho}}{X_2} - \frac{X_1 \frac{(\epsilon_1 - 1)}{\epsilon_1 + 2} \cdot \frac{M_1}{\rho_1}}{X_2}$$

$$= \frac{\epsilon - 1}{\epsilon + 2} \frac{M_2}{\rho} + \frac{\epsilon - 1}{\epsilon + 2} \frac{X_1 M_1}{\rho} \cdot \frac{1}{X_2} - \frac{X_1 \frac{(\epsilon_1 - 1)}{(\epsilon_1 + 2)} \cdot \frac{M_1}{\rho_1}}{X_2}$$

$$= \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M_2}{\rho} + \frac{X_1 M_1}{X_2}\left(\frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{1}{\rho} - \frac{\epsilon_1 - 1}{\epsilon_1 + 2} \cdot \frac{1}{\rho_1}\right) \qquad (4)$$

$$\epsilon = \epsilon_1 (1 + \alpha X_2) \qquad (5)$$
$$\rho = \rho_1 (1 + \beta X_2)$$

Substituting (5) into the second half of (4),

$$\mathcal{P}_2 = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M_2}{\rho} + \frac{X_1 M_1}{X_2} \frac{(\epsilon_1 + \alpha \epsilon_1 X_2 + 1)}{(\epsilon_1 + \alpha \epsilon_1 X_2 + 2)} \cdot \frac{1}{\rho} - \frac{\epsilon_1 - 1}{\epsilon_1 + 2} \cdot \frac{1}{\rho_1}$$

Appendix IV (cont.)

$$P_2 = \frac{\epsilon-1}{\epsilon+2}\cdot\frac{M_2}{\rho} + \frac{x_1 M_1}{x_2}\left[\frac{(\epsilon_1+\alpha\epsilon_1 x_2-1)(\epsilon_1+2)(\rho_1)-(\epsilon_1-1)(\epsilon_1+\alpha\epsilon_1 x_2+2)(\rho_1)(1+\beta x_2)}{(\epsilon_1+\alpha\epsilon_1 x_2+2)(\rho)(\epsilon_1+2)(\rho_1)}\right]$$

$$= \frac{\epsilon-1}{\epsilon+2}\cdot\frac{M_2}{\rho} + \frac{x_1 M_1}{x_2}\left[\frac{(\epsilon_1+\alpha\epsilon_1 x_2-1)(\epsilon_1+2)-[(\epsilon_1-1)(\epsilon_1+\alpha\epsilon_1 x_2+2)]-[(\epsilon-1)(\epsilon_1+\alpha\epsilon_1 x_2+2]}{(\epsilon_1+\alpha\epsilon_1 x_2+2)(\rho)(\epsilon_1+2)(\rho_1)}\right]$$

$$= \frac{\epsilon-1}{\epsilon+2}\cdot\frac{M_2}{\rho} + \frac{x_1 M_1}{\rho}\left[\frac{3\alpha\epsilon_1-\beta(\epsilon_1-1)[\epsilon_1-\alpha\epsilon_1 x_2+2]}{[\epsilon_1(1+\alpha x_2)+2][\epsilon_1+2]}\right] \qquad (6)$$

$$\lim_{x_2\to 0} P_2 = P_\infty, \quad \lim_{x_2\to 0}\epsilon = \epsilon_1, \quad \lim_{x_2=0}\rho = \rho_1, \quad \lim_{x_2\to 0} x_1 = 1$$

$$P_\infty = \frac{\epsilon_1-1}{\epsilon_1+2}\cdot\frac{M_2}{\rho_1} + \frac{M_1}{\rho_1}\frac{[3\alpha\epsilon_1-\beta(\epsilon_1-1)(\epsilon_1+2)]}{\rho_1(\epsilon_1+2)^2}$$

$$= \left(\frac{\epsilon_1-1}{\epsilon_1+2}\cdot\frac{M_2}{\rho_1}\right) + \frac{3M_1\alpha\epsilon_1}{\rho_1(\epsilon_1+2)^2} - \frac{M_1(\beta)(\epsilon-1)}{\rho_1(\epsilon_1+2)}$$

$$= \frac{\epsilon-1}{\epsilon_1+2}\cdot\frac{M_2-\beta M_1}{\rho_1} + \frac{3M_1\alpha\epsilon_1}{\rho_1(\epsilon_1+2)^2}$$

$$P_\infty = A\cdot\left(M_2-\beta\rho_1\cdot\frac{M_1}{\rho_1}\right)+B\cdot\alpha\epsilon_1 \qquad (7)$$

where $A = \frac{\epsilon_1-1}{\epsilon_1+2}\cdot\frac{1}{\rho_1}$ $\quad B = \frac{3M_1}{\rho_1(\epsilon_1+2)^2}$

Appendix IV (cont.)

A similar derivation can be used for concentration:

$$\epsilon = \epsilon_1 (1 + \alpha' c)$$
$$\rho = \rho_1 (1 + \beta' c) \qquad 5a$$

Inserting into equation 4 and rearranging:

$$P_2 = \frac{\epsilon - 1}{\epsilon + 2} \frac{M_2}{\rho} + \frac{X_1 M_1}{X_2 \rho} \cdot \frac{c\left[3\alpha'\epsilon_1 - \beta'(\epsilon_1 - 1)\left[\epsilon_1(1 + \alpha' c) + 2\right]\right]}{\left[\epsilon_1(1 + \alpha' c) + 2\right]\left[\epsilon_1 + 2\right]} \qquad (8)$$

Substituting into (8) the relation

$$\frac{X_1 M_1}{X_2} = \frac{1000\rho - cM_2}{c}$$

and extrapolating to P_∞ as before,

$$P_\infty = \frac{\epsilon_1 - 1}{\epsilon_1 + 2} \cdot \frac{M_2 - 1000\beta'\rho_1}{\rho_1} + \frac{3000\alpha'\epsilon_1}{(\epsilon_1 + 2)^2}$$

$$= A \cdot (M_2 - 1000\beta'\rho_1) + C \cdot \alpha' \epsilon_1$$

where $A = \frac{\epsilon_1 - 1}{\epsilon_1 + 2} \cdot \frac{1}{\rho_1}$ and $C = \frac{3000}{(\epsilon_1 + 2)^2}$

Appendix V
Instructions for Operation of the Heterodyne Beat Circuit

1. All wires should be checked between the three chassis boxes to make sure there are no shorts.

2. Connections of coaxial leads from one box to the next, as explained on the instrument, should be checked. The connection to the scope should be to the vertical input.

3. The switch on the front of the resonance circuit should be switched to the right.

4. Check to make sure that the cell is connected to the circuit and that the Pt wires from the cell are not touching.

5. The instrument is turned on by turning on both the heater and the high voltage in the power supply. A voltage of 250 V should be applied.

6. Both the instrument and the oscilloscope should be allowed to warm up for at least 30 minutes prior to use.

7. With capacitor 1,2, fully closed, gradually decrease the capacitance (in the fixed frequency oscillator) until the ammeter reaches a low current reading of about 1.5 ma. Continue to decrease it until the current has risen to about 3 ma. This is the point of maximum stability in the oscillator.

8. Carefully turn the precision capacitor until the vernier reads 0.000 in the range of 78-80 on the coarse vernier. Be sure to turn the vernier slowly as the dial will skip numbers if it is turned too fast.

9. With the vernier reading 0.000, adjust the coarse capacitor until the circuit is at approximately zero beat. This will appear as a solid band on the oscilloscope, which should be set to read in the range of .5 millisec / cm. Immediately before and after the zero beat point, sinusoidal waves will appear on the scope. When the beat frequency is quite high, a fuzzy band will appear about two times the size of the zero beat band.

10. Fill the cell with the dielectric, making sure that the plates are completely covered with liquid.

Appendix V (cont.)

11. Readjust the circuit to zero beat.

12. Take the reading of the precision vernier, which equals the ΔC for the dielectric.

Appendix Va
Instructions for Operation of the Resonance Circuit

1. Connect the leads from the resonance circuit to the Pt wires from the cell.

2. Connect both the heater and the B+ voltage leads to the power supply. It is a good idea to disconnect the heterodyne beat circuit from the power supply when using the resonance circuit.

3. Switch the switch on the front of the resonance circuit to the left.

4. Instructions 4-6, 8-12 for the heterodyne beat circuit apply when using this circuit.

Appendix VI
Troubleshooting

(The problem will be listed first, then the possible solution.)

1. Circuit will not tune to zero beat. Band remains fuzzy. Check to see that the switch on the resonance circuit front is to the right.

2. Circuit is tuned to zero beat without cell, but when the cell is connected, adjustment of the precision capacitor results in no change.
   Possible short in Pt wires of cell. If both are touching metal surfaces which are connected, such as the sides of a clamp, short will exist.

3. Thin diagonal line appears on scope.
   Check to see that the ground lead from the mixer chassis is connected.

4. Ammeter reading is zero.
   This is due to a problem in the fixed frequency oscillator. Check to see that the external wires are not shorted.
   Check also capacitor 1,2 to see that the plates are not touching. Further troubleshooting must be done in the inner circuitry.

Appendix VI (cont.)

5. Inner circuitry of fixed frequency oscillator non-functional.
With a grid-dip meter check to see if the circuit can be tuned to resonance (this is done with the power off). Using a r.f. detector, check to see if a r.f. signal is being given off with the power on. No r.f.signal indicates possible crystal failure. The crystal can be tested by placing it in the resonance circuit.

6. Crystal is operative but circuit is not.
Check all inner leads to see that they are not shorted. Check connections to coil to see that they are not broken.
Test with a VOM the individual resistors. One which offers an infinite resistance is burned out. Check capacitors for shorts.

7. No short in cell but adjustment of the precision capacitor results in no change on the scope.
Possible problem in the variable frequency oscillator. Connect the v.f.o. output to the vertical input of the scope to determine if it is operating.

8. No output from v.f.o.
See #6.

Appendix VIa
The Grid-dip Meter

A grid-dip meter is a simple vacuum tube oscillator with an ammeter for reading grid current. It can be easily coupled (usually through the inductor of the circuit being tested). When the external circuit and the grid-dip meter are tuned to the same frequency, the external circuit will absorb energy from the grid-dip oscillator circuit. A corresponding sharp drop in grid current will take place. The point at which the second circuit is tuned to the same frequency as the grid-dip meter can thus be easily read, and since the frequency for the grid-dip meter is known, it can be determined for the unknown circuit.

Appendix VII
Specifics for Solutions

Both the Guggenheim and Halverstadt-Kumler methods of determining dipole moments in solution are extensions of Debye theory and assume negligible interaction between molecules. For liquids this state is only approached in very dilute solutions. Concentrations for solutions should thus be very small, on the order of 1-5 mole per cent.

The accuracy of the instrument limits the degree of dilution possible; the concentration must be great enough to produce a measureable change in the capacitance of the cell. The best procedure when using the precision capacitor currently available is to test different solutions to determine the maximum dilution for which measurement is possible.

Both solute and solvent must be thoroughly purified before use. A good solvent is one which is easy to handle and will present little danger of solute-solvent interaction. It must of necessity be non-polar. Perhaps the best hydrocarbon solvent is cyclohexane, which can easily be distilled, is non-polar, and can be dried over sodium. Benzene and carbon tetrachloride are also used as solvents if cyclohexane is unsuitable. One disadvantage of benzene is that with its π bonds, it can associate with organic and inorganic compounds.

In the preparation of the solutions, care must be taken to prevent the absorption of moisture. Water is polar and can associate with itself or with the solute; a significant error can thus be introduced if water is absorbed. In addition an effort must be made to prepare and handle all solutions in the same manner. Any error introduced will be common to the entire set of data. Preparation of solutions by successive dilution is not recommended since each solution will be given slightly different treatment. For a more detailed discussion of dipole moment measurements of solutions, see reference (13).

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(11) [illegible]

(12) [illegible]

(13) [illegible], B., [illegible]

(14) [illegible]

(15) [illegible], [illegible]

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BASIC SOLMOM

```
10 PRINT
20 PRINT "CALCULATION OF DIPOLE MOMENT FOR SOLUTION"
30 PRINT "     HALVERSTADT-KUMLER METHOD"
40 PRINT
140 PRINT "D STANDS FOR DIELECTRIC CONSTANTS OF SOLUTION"
150 PRINT
160 PRINT "X(2) STANDS FOR MOLE FRACTIONS OF SOLUTE"
170 PRINT
171 PRINT "INPUT NUMBER OF TIMES CALCULATION IS DESIRED"
172 INPUT H(1)
173 PRINT
174 FOR H=1 TO H(1)
180 PRINT "INPUT NUMBER OF PAIRS OF X(2), D"
190 INPUT N
200 PRINT
210 PRINT "INPUT X(2), D, ONE PAIR PER LINE"
220 FOR Q=1 TO 2
230 LET A=0
240 LET B=0
250 LET C=0
260 LET D=0
270 FOR J=1 TO N
280 INPUT X(J), Y(J)
281 PRINT
285 LET A=A+X(J)
290 LET B=B+Y(J)
300 LET C=C+X(J)*Y(J)
310 LET D=D+(X(J)↑2)
320 NEXT J
325 LET G=N
330 LET O=A↑2-(G*D)
360 P(Q)=(A*B-G*C)/O
365 IF Q=2 GO TO 435
370 PRINT "P STANDS FOR DENSITY OF SOLUTION"
390 PRINT "INPUT X(2), P, ONE PAIR PER LINE"
400 PRINT
411 NEXT Q
435 PRINT "ENTER DIELECTRIC CONSTANT OF SOLVENT"
440 INPUT D(1)
442 PRINT
444 PRINT "ENTER DIELECTRIC CONSTANT OF SOLUTE"
450 INPUT D(2)
455 PRINT
460 PRINT "ENTER DENSITY OF SOLVENT"
465 INPUT S(1)
470 PRINT
475 PRINT "ENTER DENSITY OF SOLUTE"
480 INPUT S(2)
490 PRINT
495 PRINT "ENTER MOLECULAR WEIGHT OF SOLVENT"
500 INPUT M(1)
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[illegible] PRINT
[illegible] PRINT "CALCULATION OF [illegible]
[illegible] PRINT "     [illegible]"
[illegible] PRINT
[illegible] PRINT "D STATUS [illegible]
[illegible] PRINT
[illegible] PRINT "X(2) STATUS [illegible]
[illegible] PRINT
[illegible] PRINT "[illegible]
[illegible] INPUT H(1)
[illegible] PRINT
[illegible] FOR H=1 [illegible]
[illegible] PRINT "[illegible]
[illegible] INPUT 1
[illegible] PRINT
[illegible] PRINT "[illegible]
[illegible] FOR H=1 [illegible]
[illegible] LET A=[illegible]
[illegible] LET B=0
[illegible] LET C=0
[illegible] LET [illegible]
[illegible] [illegible]
[illegible] [illegible]
[illegible] LET A=A+X(H)
[illegible] [illegible]
[illegible] LET C=C+X(H)
[illegible] LET [illegible]
[illegible] [illegible]
[illegible] LET [illegible]
[illegible] P(H)=[illegible]
[illegible] IF [illegible]
[illegible] [illegible]
[illegible] [illegible]
[illegible] [illegible]
[illegible] [illegible]
[illegible] PRINT "[illegible]"
[illegible] INPUT D(1)
[illegible] PRINT
[illegible] PRINT "[illegible] OF [illegible]"
[illegible] INPUT D(2)
[illegible] PRINT
[illegible] PRINT "[illegible] LIMIT OF S [illegible]"
[illegible] INPUT S(1)
[illegible] PRINT
[illegible] PRINT "[illegible] DENSITY OF [illegible]"
[illegible] INPUT E(2)
[illegible] PRINT
[illegible] PRINT "[illegible] " [illegible]
[illegible] INPUT M(1)
```

```
510 PRINT
515 PRINT "ENTER MOLECULAR WEIGHT OF SOLUTE"
520 INPUT M(2)
525 PRINT
530 T=(D(1)-1)/(D(1)+2)
540 T(1)=T/S(1)
550 T(2)=T(1)*M(2)-T(1)*M(1)*P(2)/S(1)
555 T(3)=3*M(1)/((D(1)+2)↑2*S(1))
556 T(4)=T(2)+T(3)*P(1)
560 PRINT "ENTER INDEX OF REFRACTION OF SOLUTE"
565 INPUT R
570 PRINT
600 W=((R↑2-1)/(R↑2+2))*M(2)/S(2)
610 PRINT "ENTER TEMPERATURE IN DEGREES KELVIN"
620 INPUT E
630 PRINT
640 K=(.0128130E-18)*SQR((T(4)-W)*E)
650 PRINT "DIPOLE MOMENT FOR ",H,"EQUALS",K
651 PRINT
654 IF H=H(1) GO TO 660
655 PRINT "CALCULATION FOR NEXT DIPOLE MOMENT VALUE"
656 PRINT
657 NEXT H
660 END
```

```
510 PRINT
515 PRINT "ENTER MOLECULAR FRACTION OF COLLIDER"
520 INPUT X(2)
525 PRINT
530 T=(D(I)-1)*(E(I)+2)
540 T(I)=T*S(I)
550 T(3)=T(I)*M(2)-T(I)*M(1)*P(2)*S(I)
555 T(3)=3*X(I)*((P(I)+2)*S*S(I))
560 T(4)=T(2)+T(3)*P(I)
565 PRINT "ENTER INDEX OF REFRACTIVE INDEX "
565 INPUT R
570 PRINT
600 W=((R*S-1)*(R*S+2))*X(2)*S(2)
610 PRINT "SAMPLE TEMPERATURE IN DEGREE KELVIN "
620 INPUT F
630 PRINT
640 K=(.01*6138E-18)*W*((.(9)-.)*F)
650 PRINT "DIPOLE MOMENT IN ";B;"EGUAL 2 ";
651 PRINT
654 IF H=H(I) GO TO 66
655 PRINT "CALCULATIONS FOR ";N;" DIPOLE ";N;" ";
656 PRINT
657 NEXT H
660 END
```

BASIC DMOM

```
10 PRINT
20 PRINT "CALCULATION OF DIPOLE MOMENT FOR PURE POLAR LIQUIDS"
25 PRINT "                    ONSAGER METHOD"
30 PRINT
40 PRINT "INPUT AFTER EXCLAMATION POINT"
43 PRINT
45 PRINT "INPUT NUMBER OF TIMES CALCULATION IS DESIRED"
46 INPUT H(1)
47 FOR H=1 TO H(1)
50 PRINT
60 PRINT "ENTER MOLECULAR WEIGHT"
70 INPUT W
80 PRINT
90 PRINT "ENTER DENSITY"
91 INPUT P
95 PRINT
100 PRINT "ENTER INDEX OF REFRACTION"
101 INPUT N
105 PRINT
110 PRINT "ENTER DIELECTRIC CONSTANT"
111 INPUT C
115 PRINT
120 PRINT "ENTER TEMPERATURE IN DEGREES KELVIN"
121 INPUT T
125 PRINT
150 LET V=W/P
160 G=(C-N)*((2)*(C)+N)
170 L=G/(C)*((N+2)↑2)
180 Q=(L)*(V)*(T)
190 M=(.0128130E-18)*SQR(Q)
200 PRINT "DHPOLE MOMENT FOR";H,"EQUALS";M
205 IF H=H(1) GO TO 210
206 PRINT "CALCULATION FOR NEXT DIPOLE MOMENT VALUE"
207 PRINT
208 NEXT H
209 PRINT
210 END
```